Neutral palladium(0) complexes from Pd(OAc)$_2$ and tri-2-furylphosphine and their reactivity in oxidative addition of iodobenzene

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Dedicated to our colleague and dear friend Professor Armand Lattes for the celebration of 50 years of teaching and research

Abstract
A Pd(0) complex, $S$Pd$_0$(TFP)$_2$ (TFP = tri-2-furylphosphine, $S$ = THF, DMF), is spontaneously formed upon addition of 3 equiv TFP to Pd(OAc)$_2$ in THF or DMF. Higher amount of TFP leads to the formation of Pd$_0$(TFP)$_3$ in equilibrium with TFP and $S$Pd$_0$(TFP)$_2$. The latter complex is the reactive species in the oxidative addition with PhI leading to trans-PhPdI(TFP)$_2$. The oxidative addition is retarded by excess TFP. Comparison with PPh$_3$ investigated in a previous work establishes that i) a neutral complex $S$Pd$_0$(TFP)$_2$ is formed rather than the anionic [Pd$_0$(PPh$_3$)$_2$(OAc)]$,^{−}$, ii) the rate of formation of $S$Pd$_0$(TFP)$_2$ is faster than that of [Pd$_0$(PPh$_3$)$_2$(OAc)]$,^{−}$, iii) $S$Pd$_0$(TFP)$_2$ is more reactive than [Pd$_0$(PPh$_3$)$_2$(OAc)]$^{−}$ in oxidative addition with PhI, iv) the oxidative addition gives the neutral trans-PhPdI(TFP) rather than trans-PhPd(OAc)PPh$_3$)$_2$. $S$Pd$_0$(TFP)$_2$ generated from Pd(OAc)$_2$ and 3 equiv TFP is much more reactive than when it generated from Pd$_0$(dba)$_2$ and 2 equiv TFP due to the non interference of Pd$_0$(dba)(TFP)$_2$.

Keywords: Palladium, oxidative addition, tri-2-furylphosphine, palladium diacetate

Introduction

We earlier established that Pd(0) complexes were generated in DMF or THF upon mixing Pd(OAc)$_2$ and excess triarylphosphines PR$_3$ (R = aryl, alkyl),$^1$ i.e., a set of precursors often used to catalyzed Heck reactions (Scheme 1).$^{2,3}$ As far as PPh$_3$ is concerned, the resulting catalytic
palladium(0) species was established to be anionic\textsuperscript{3} \([\text{Pd}^0(\text{PPh}_3)_2(\text{OAc})]^-\) and this structure was further confirmed by DFT calculations (Scheme 1).\textsuperscript{4}

\[
\begin{align*}
\text{PhI} + \text{Ph} + \text{NEt}_3 & \quad \xrightarrow{\text{Pd(OAc)}_2 + n \text{L}} \quad \text{Ph} + \text{HNEt}_3^+ + \text{I}^- \\
\text{Pd(OAc)}_2 + 3\text{PPh}_3 & \quad \xrightarrow{\text{DMF, 25 } ^\circ\text{C}} \quad \text{Pd}^0\text{L(OAc)}^- \\
& \quad \xrightarrow{\text{Ph}^+} \quad \text{Pd}^0\text{L}_2(\text{OAc})^- \\
& \quad \xrightarrow{\text{PhI}} \quad \text{PhPd(OAc)}L_2 \quad \xrightarrow{\text{oxidative addition}} \quad \text{PhPdL}_2^+ + \text{AcO}^- \\
& \quad \xrightarrow{\text{carbopalladation}} \quad \text{PhPdL}_2^+ + \text{AcO}^- \\
\end{align*}
\]

\textbf{Scheme 1}

The oxidative addition of \([\text{Pd}^0(\text{PPh}_3)_2(\text{OAc})]^-\) with iodobenzene gives the unexpected \textit{trans}-PhPd(OAc)(PPh)_3 which proved to be a key complex involved in the rate determining step of Heck reactions, i.e., in the carbopalladation step with alkenes (Scheme 1).\textsuperscript{3} Indeed, \textit{trans}-PhPd(OAc)(PPh)_3 was found to be much more reactive with the alkene than \textit{trans}-PhPdI(PPh)_3 which is usually formed in the oxidative addition of PhI with the neutral complex \text{Pd}^0(PPh)_3. The efficient interference of the ions AcO\textsuperscript{−} delivered by the precursor Pd(OAc)_2 in Heck reactions was then clearly established (Scheme 1).\textsuperscript{3}

The ligand tri-2-furylphosphine (TFP) has been used by Farina \textit{et al.} in Palladium-catalyzed Stille reactions based upon using \text{Pd}^0(\text{dba})_2 or \text{Pd}^0_2(\text{dba})_3 as precursors.\textsuperscript{5} The structure and reactivity of the ensuing Pd(0) complex in oxidative addition with iodobenzene has been fully investigated in our group leading to the identification of \text{SPd}^0(\text{TFP})_2 (S = \text{THF, DMF}) as the
reactive complex (Scheme 2). In DMF, such Pd(0) complex was found to be more reactive than the corresponding Pd(0) complexes ligated by PPh\textsubscript{3} when considering overall identical concentrations of the two ligands.

\[
Pd^{0}(\text{dba})_{2} + 2 \text{TFP} \rightarrow Pd^{0}(\text{dba})(\text{TFP})_{2} + \text{dba}
Pd^{0}(\text{dba})(\text{TFP})_{2} \leftrightarrow Pd^{0}(\text{TFP})_{2} + \text{dba}
Pd^{0}(\text{TFP})_{2} + \text{TFP} \leftrightarrow Pd^{0}(\text{TFP})_{3}
Pd^{0}(\text{TFP})_{2} + \text{PhI} \rightarrow \text{trans-PhPdI(TFP)_{2}}
\]

Scheme 2 (the solvent THF or DMF on low-ligated Pd\textsuperscript{0} complexes is voluntarily omitted)

The ligand TFP may also be introduced in Palladium-catalyzed reactions upon using Pd(OAc)\textsubscript{2} as the precursor. We report herein that Pd(0) complexes are indeed generated from mixtures of Pd(OAc)\textsubscript{2} and tri-2-furylphosphine. In unexpected contrast with the case of PPh\textsubscript{3}, upon using TFP, the ensuing Pd(0) complex is no longer anionic and consequently its oxidative addition with PhI does not provide trans-PhPd(OAc)(TFP)\textsubscript{2} but the classical trans-PhPdI(TFP)\textsubscript{2}.

**Results and Discussion**

**Evidence for the formation of Pd(0) complexes from Pd(OAc)\textsubscript{2} and n TFP (n ≥ 3) in THF or DMF**

As performed previously for PPh\textsubscript{3},\textsuperscript{1,3} the reaction of Pd(OAc)\textsubscript{2} with n equiv of TFP (n ≥ 3) was followed by \textsuperscript{3}P NMR spectroscopy in THF containing 10 % acetone-\textit{d}\textsubscript{6} for the lock.\textsuperscript{1} After addition of n = 10 equivalents of TFP to a solution of Pd(OAc)\textsubscript{2} (16 mM) in THF, two main signals were observed: a sharp singlet at \(\delta_{1} = -14.32\) ppm, assigned to tri-2-furylphosphine oxide TFP(O) by comparison to an authentic sample and a broad signal at \(\delta_{2} = -66.64\) ppm (\(\Delta\nu/2 = 460\) Hz). The signal of the free TFP at \(\delta_{0} = -75.63\) ppm was not observed, suggesting that it was involved in an equilibrium with Pd(0) complexes being then responsible for the broad signal at \(\delta_{2}\). After addition of PhI (1 equiv), the broad signal at \(\delta_{2}\) was no longer observed confirming that \(\delta_{2}\) did effectively belong to Pd(0) complexes ligated by TFP. A new sharp singlet appeared at \(\delta_{3} = -28.22\) ppm. It was assigned to trans-PhPdI(TFP)\textsubscript{2} by comparison to an authentic sample.\textsuperscript{6} The signal of the free TFP at \(\delta_{0}\) was also restored.

The complex Pd\textsuperscript{0}(TFP)\textsubscript{3} generated from Pd\textsuperscript{0}(dba)\textsubscript{2} after addition of excess TFP was characterized in a previous work by \textsuperscript{3}P NMR as a broad signal at −64.46 ppm in THF, due to the equilibrium between Pd\textsuperscript{0}(TFP)\textsubscript{3}, Pd\textsuperscript{0}(TFP)\textsubscript{2} and TFP (third equation in Scheme 2).\textsuperscript{6} Consequently, the broad signal at \(\delta_{3}\) characterizes a similar equilibrium. This suggests that Pd\textsuperscript{0}(TFP)\textsubscript{3} undergoes oxidative addition with PhI via Pd\textsuperscript{0}(TFP)\textsubscript{2}, as established in Scheme 2 (third and fourth equation). Those Pd(0) complexes have thus been generated in a fast reaction
(within less than 20 min, the time required for recording the first $^{31}$P NMR spectrum) from the mixture: Pd(OAc)$_2$ + 10 TFP. The primary complex Pd(OAc)$_2$(TFP)$_2$ was not detected by $^1$P NMR due to its too short life but was characterized in cyclic voltammetry by its reduction peak ($E^0 = -0.96$ V vs SCE) recorded 5 min after mixing, just before its fast evolution to Pd(0) complexes (Scheme 3).

![Scheme 3](image)

**Scheme 3** (The solvent THF or DMF on low-ligated Pd$^0$ complexes is voluntarily omitted)

The complex trans-PhPdI(TFP)$_2$ was formed in the oxidative addition and not trans-PhPd(OAc)(TFP)$_2$ as expected if anionic $[Pd^0(TFP)_{n'}(OAc)]^-$ ($n' = 2, 3$) had been formed and involved in the oxidative addition. Moreover, I$^-$ ions were not released during the oxidative addition step, as it occurred for the oxidative addition of $[Pd^0(PPh_3)_2(OAc)]^-$ (Scheme 1).$^3$ This suggests that complexes $Pd^0(TFP)_{n'}$ ($n' = 2, 3$) generated from Pd(OAc)$_2$(TFP)$_2$ are neutral and not coordinated by the acetate ion (Scheme 3). It is only upon addition of large excess AcO$^-$ (10 equiv nBu$_4$NOAc) that trans-PhPdI(TFP)$_2$ partially disappeared in THF to afford a new complex characterized by a singlet at $\delta_1 = -23.64$ ppm and assigned to trans-PhPd(OAc)(TFP)$_2$ formed in 34 % yield (Scheme 4). The same complex trans-PhPd(OAc)(TFP)$_2$ was formed upon addition of AcO$^-$ (10 equiv.) to the isolated trans-PhPdI(TFP)$_2$ complex generated through the sequence of reactions in Scheme 2. This shows that the equilibrium of Scheme 4 lies in favor of trans-PhPdI(TFP)$_2$ for low ratio [AcO$^-$/trans-PhPdI(TFP)$_2$].

![Scheme 4](image)

**Scheme 4**

The formation of a Pd(0) complex from Pd(OAc)$_2$ and 4 TFP in DMF was followed by cyclic voltammetry. This allows the characterization and titration of Pd(II) or Pd(0) complexes at
times shorter than those required to obtain a first $^{31}$P NMR spectrum. A yellow solution is formed after addition of TFP (8 mM) to a brown solution of Pd(OAc)$_2$ (2 mM) in DMF containing $n$Bu$_4$NBF$_4$ (0.3 M). An irreversible reduction peak at $E_{p,R1}^o = -0.12$ V vs SCE is then observed in the first recorded CV (2 min after mixing) assigned to Pd(OAc)$_2$(TFP)$_2$. This reduction peak disappeared with time and an irreversible oxidation peak was then observed at $E_{p,O1}^o = +0.36$ V vs SCE when the CV was performed directly to oxidation, attesting to the formation of a Pd(0) complex from Pd(OAc)$_2$(TFP)$_2$. Accordingly, this oxidation peak current increased with time (Fig 1a) but was no longer observed after addition of PhI (2 mM). In a previous work, the Pd(0)(TFP)$_3$ complex generated together with Pd(0)(dba)(TFP)$_2$ after addition of TFP (8 mM) to Pd(0)(dba)$_2$ (2 mM) in DMF (Scheme 2) had been characterized by an oxidation peak at +0.36 V, thus identical to the oxidation peak potential of the Pd(0) observed above, generated from Pd(OAc)$_2$ + 4 TFP.

![Figure 1](image)

**Figure 1.** a) Cyclic voltammetry of Pd(0)(TFP)$_3$ generated from Pd(OAc)$_2$ (2 mM) and 4 equiv TFP in DMF containing $n$Bu$_4$NBF$_4$ (0.3 M) versus time. 1: 5 min; 2: 23 min; 3: 26 min. Steady gold disk electrode (d 0.5 mm), scan rate: 0.2 Vs$^{-1}$. b) Kinetics of the formation of Pd(0)(TFP)$_3$ generated from Pd(OAc)$_2$ (2 mM) and 10 equiv TFP in DMF containing $n$Bu$_4$NBF$_4$ (0.3 M). Plot of lnχ (χ = $i_{lim}$ - $i_t$)/$i_{lim}$ against time.

The rate of formation of the Pd(0) complex from Pd(OAc)$_2$ + 10 TFP was determined in DMF by amperometry at a rotating disk electrode polarized at +0.4 V, on the plateau of the oxidation wave of the Pd(0) complex, as done in the case of PPh$_3$. The increase of the oxidation plateau current (proportional to the Pd(0) concentration) was recorded with time until a limiting value was observed, attesting to the end of the reaction. The plot of lnχ (χ = $i_{lim}$ - $i_t$)/$i_{lim}$; $i_{lim}$: final oxidation current; $i_t$: oxidation current at t) against time gave two straight lines (Fig 1b) as
in the case of PPh$_3$, due to the formation of an intermediate low-ligated Pd(0) complex before its final stabilization by an extra ligand leading to Pd$^0$(TFP)$_3$ (Scheme 3). The rate constant $k_0$ (Scheme 3) for the formation of the Pd(0) complex was determined from the slope of the straight line obtained at longest times:

$$k_0 = 7.2 \times 10^{-3} \text{ s}^{-1} \text{ (DMF 25 °C)}.$$

All these results confirm that the reactions proposed in Scheme 3 take place in DMF and THF. A Pd$^0$ complex is generated from Pd(OAc)$_2$(TFP)$_2$ in a fast reaction.

**Kinetics and mechanism of the oxidative addition of PhI to the Pd(0) complexes generated from Pd(OAc)$_2$ and n TFP ($n \geq 3$) in THF or DMF**

When 1 equiv PhI was added to the Pd$^0$(TFP)$_2$ generated from Pd(OAc)$_2$ ($C_0 = 2$ mM) associated to 3 equiv TFP in DMF containing nBu$_4$NBF$_4$ (0.3 M), the oxidation plateau current of Pd$^0$(TFP)$_2$ (proportional to its concentration) decreased due to the oxidative addition process (Scheme 5). The kinetics of the oxidative addition was then followed by amperometry at a rotating disk electrode polarized at +0.4 V on the plateau of the oxidation wave of Pd$^0$(TFP)$_2$, by recording the decrease of the oxidation plateau current until total conversion.

$$\text{Pd(OAc)$_2$ + 3TFP + H$_2$O } \xrightarrow{k_0} \text{Pd}^0(\text{TFP)$_2$ + AcO}^- + H^+ + \text{TFP(O) + AcOH}$$

$$\text{Pd}^0(\text{TFP)$_2$ + PhI } \xrightarrow{k} \text{trans-PhPdI(TFP)$_2$}$$

**Scheme 5**

Under stoichiometric conditions, the kinetic law is given in Eq 1 ($x = \text{[Pd}^0]/\text{[Pd}^0]_0 = i_i/i_0$; $i_i$: oxidation current of Pd$^0$(TFP)$_2$ at t, $i_0$: initial oxidation current).

$$\frac{1}{x} = kC_0t + 1 \quad (1)$$

The plot of $1/x$ against time was linear (Fig 2a) establishing a first order reaction for Pd$^0$(TFP)$_2$ and PhI. The rate constant $k$ was determined from the slope of the straight line according to Eq 1.

$$k = 99 \text{ (±2) M}^{-1}\text{s}^{-1} \text{ (DMF, 25 °C)}$$

The effect of acetate ions was tested by adding 10 equiv AcO$^-$ to the Pd(0) generated from Pd(OAc)$_2 + 3$ TFP before introduction of PhI. From the value of $t_{1/2}$ given in Table 1, one deduce that the kinetics was not significantly affected by the added acetate ions, establishing definitively that Pd$^0$(TFP)$_2$ generated from Pd(OAc)$_2$ associated with 3 equiv TFP did not equilibrate significantly with acetate ions in DMF.

A similar experiment was performed starting from Pd$^0$(TFP)$_3$ generated from Pd(OAc)$_2$ ($C_0 = 2$ mM) and 10 equiv TFP in DMF. From the half reaction $t_{1/2}$ given in Table 1, one notes that the oxidative addition of PhI was slower due to the excess of ligand (6 free equivalents after reaction) and the formation of the unreactive Pd$^0$(TFP)$_3$ (Scheme 6). The kinetic law is given in Eq 2.
Scheme 6

\[ 1/x = kKC_0/[\text{TFP}] + 1 \]  

\( kK = 0.01 \text{ s}^{-1} \) was determined from the slope of the straight line obtained by plotting \( 1/x \) against time (Fig 2b). Since \( k = 99 \text{ M}^{-1}\text{s}^{-1} \) is known (vide supra), the equilibrium constant \( K = ([\text{Pd}^0(\text{TFP})_2][\text{TFP}]/[\text{Pd}^0(\text{TFP})_3])_{\text{eq}} \) could be determined.

\[ K = 1 \times 10^{-4} \text{ M (DMF, 25 °C)} \]

Figure 2. Kinetics of the oxidative addition of PhI (2 mM) with Pd\(^0\)(TFP)\(_2\) generated from Pd(OAc)\(_2\) (2 mM) and \( n \) equiv TFP in DMF containing \( n\text{Bu}_4\text{NBF}_4 \) (0.3 M) at 25 °C. Plot of \( 1/x \) against time: a) \( n = 3 \); b) \( n = 10 \).

Similar procedure was used to follow the kinetics of the oxidative addition in THF (Table 1). Under similar concentrations, the oxidative addition performed from Pd\(^0\)(TFP)\(_2\) generated from Pd(OAc)\(_2\) \( (C_0 = 2 \text{ mM}) \) associated with 3 equiv TFP was found to be faster in THF than in DMF leading to less accurate data for the determination of \( k \) (Table 1). This suggests a coordination of Pd\(^0\)(TFP)\(_2\) by DMF since this is expected to be stronger than by THF. In THF,
the oxidative addition proceeded also slower in presence of excess TFP \((n = 10)\) (Table 1) as in DMF, due to the formation of the non reactive \(\text{Pd}^0(\text{TFP})_3\).\(^6\)

**Table 1.** Kinetic and thermodynamic data for the oxidative addition of PhI (2 mM) with \(\text{Pd}^0(\text{TFP})_2\) generated from \(\text{Pd(OAc)}_2\) (2 mM) and \(n\) TFP \((n = 3\) or 10\) in THF or DMF. See Schemes 5 and 6 for the definition of \(k\) and \(K\).

<table>
<thead>
<tr>
<th>Precursor of (\text{Pd}^0)</th>
<th>(t_{1/2}) (s)</th>
<th>(k) (M(^{-1})s(^{-1}))</th>
<th>(kK) (s(^{-1}))</th>
<th>(K) (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Pd(OAc)}_2 + 3) TFP</td>
<td>5.1</td>
<td>(~1)</td>
<td>99±2</td>
<td>500±200</td>
</tr>
<tr>
<td>(\text{Pd(OAc)}_2 + 10) TFP</td>
<td>556</td>
<td>190</td>
<td>-</td>
<td>0.01</td>
</tr>
<tr>
<td>(\text{Pd(OAc)}_2 + 3) TFP + 10 AcO(^-)</td>
<td>4.6</td>
<td>n.d.</td>
<td>-</td>
<td>1×10(^{-4})</td>
</tr>
</tbody>
</table>

It is worthwhile to note that the kinetics of the oxidative addition of PhI (1 equiv) with the \(\text{Pd}(0)\) complexes generated from \(\text{Pd(OAc)}_2\) (2 mM) and TFP (6 mM) in THF or DMF was not affected when performed in the presence of \(\text{NEt}_3\) (6 mM). This contrasts with the decelerating effect of \(\text{NEt}_3\) observed for the anionic \([\text{Pd}^0(\text{PPh}_3)_2(\text{OAc})]\)\(^{-}\) generated from \(\text{Pd(OAc)}_2\) (2 mM) and \(\text{PPh}_3\) (6 mM).\(^3\) This effect was rationalized as a stabilization of \([\text{Pd}^0(\text{PPh}_3)_2(\text{OAc})]\)\(^{-}\) vis à vis its decomposition to the more reactive \(\text{Pd}^0(\text{PPh}_3)_2\) and \(\text{OAc}^-\), which is a consequence of the interaction of \(\text{OAc}^-\) with \(\text{H}^+\) generated together with \([\text{Pd}^0(\text{PPh}_3)_2(\text{OAc})]\)\(^{-}\) (Scheme 1).\(^3\) The non effect of \(\text{NEt}_3\) in the case of the TFP ligand is henceforth an indirect proof that the \(\text{Pd}(0)\) complex generated from \(\text{Pd(OAc)}_2\) and TFP is definitively not ligated by an acetate ion but is neutral: \(\text{SPd}^0(\text{TFP})_2\) \((S = \text{THF} \text{ or DMF})\), as well as our former rationalization of the role of \(\text{NEt}_3\) in the \(\text{PPh}_3\) case.\(^3\)

**Conclusion: Comparison TFP/PPh3**

A palladium(0) complex is generated upon addition of TFP or \(\text{PPh}_3\) to \(\text{Pd(OAc)}_2\) by an intramolecular reduction of the \(\text{Pd}(II)\) center by the ligand in \(\text{Pd(OAc)}_2(\text{TFP})_2\) or \(\text{Pd(OAc)}_2(\text{PPh}_3)_2\) respectively with formation of the corresponding phosphine oxide. The formation of the \(\text{Pd}(0)\) complex from \(\text{Pd(OAc)}_2\) associated to \(n\) equiv TFP \((n \geq 3)\) is faster \((k_0 = 7.2×10^{-3}\) s\(^{-1}\)) than that involving \(\text{PPh}_3\) \((k_0 = 4.1×10^{-4}\) s\(^{-1}\))\(^1\) in DMF at 25 °C. From the relative position of the reduction peaks potential of \(\text{Pd(OAc)}_2(\text{TFP})_2\) \((-0.12\) V\) and \(\text{Pd(OAc)}_2(\text{PPh}_3)_2\) \((-1.23\) V\) determined in DMF,\(^1\) one observes that TFP is prone to be less
electron rich than PPh₃. Accordingly, the intramolecular reduction proceeding via the attack of the acetate onto the ligand L of Pd(OAc)₂L₂ (Schemes 1 and 3) should be indeed easier for TFP than for PPh₃, as observed experimentally.

The structure of the resulting Pd(0) complex generated from Pd(OAc)₂ + 3 equiv L differs: formation of neutral complexes SPd⁰(TFP)₂ (S = THF or DMF) in contrast to the anionic complex [Pd⁰(PPh₃)₂(OAc)]⁻. In DMF at 25 °C, at identical PhI concentration and in presence of NEt₃, SPd⁰(TFP)₂ was found to be more reactive than [Pd⁰(PPh₃)₂(OAc)]⁻ (k = 99 M⁻¹s⁻¹ and 65 M⁻¹s⁻¹ respectively). However, in absence of NEt₃, due to the partial involvement of Pd⁰(PPh₃)₂ from [Pd⁰(PPh₃)₂(OAc)]⁻, SPd⁰(TFP)₂ was found to be less reactive (k = 140 M⁻¹s⁻¹ and 99 M⁻¹s⁻¹ respectively), which can be rationalized again by the fact that TFP is a less electron-rich ligand than PPh₃. Complexes trans-PhPd(OAc)(PPh₃)₂ and trans-PhPdI(TFP)₂ are formed in the oxidative addition of PhI with the Pd(0) complexes generated from Pd(OAc)₂ associated with PPh₃ and TFP respectively. trans-PhPd(OAc)(TFP)₂ is only formed in presence of acetate ions with may be introduced as a base in Heck reactions.

At identical concentrations of the precursors and PhI, the complex SPd⁰(TFP)₂ generated from Pd(OAc)₂ + 3 TFP is much more reactive than when it generated from Pd⁰(dba)₂ + 2 TFP in THF or DMF, due to the involvement of the unreactive Pd⁰(dba)(TFP)₂ in the overall mechanism in the latter case. These results stress once more time the important role of the precursor of the Pd(0) active in catalytic cycles. Indeed the precursor controls the structure and reactivity of the Pd(0) in oxidative additions as well as the structure and reactivity of the aryl-palladium(II) complexes formed in the oxidative addition.

**Experimental Section**

**General Procedures.** ³¹P NMR spectra were recorded on a Bruker spectrometer (101 MHz) in DMF or THF containing 10% of acetone-d₆. Cyclic voltammetry was performed with a home made potentiostat and a wave form generator Radiometer-Tacussel GSTP4. The cyclic voltammograms were recorded on a Nicolet 301 oscilloscope.

**Chemicals.** DMF was distilled from calcium hydride under vacuum and kept under argon. THF was distilled from sodium-benzophenone. Pd(OAc)₂, PhI, nBu₄NOAc, nBu₄NBF₄, tri-2-furylphosphine, NEt₃ were commercial. Trans-PhPdI(TFP)₂ was synthesized according to literature. The electrochemical set-up and electrochemical procedure for voltammetry. Experiments were carried out in a three-electrode thermostated cell (25 °C) connected to a Schlenk line. The reference was a saturated calomel electrode (Radiometer) separated from the solution by a bridge filled with 3 mL of DMF containing nBu₄NBF₄ (0.3 M). The counter electrode was a platinum wire of ca. 1 cm² apparent surface area. 15 mL of DMF or THF containing n-Bu₄NBF₄ (0.3 M) were introduced into the cell followed by 21 mg (0.09 mmol) of TFP and 6.7 mg (0.03 mmol) of
Pd(OAc)$_2$. Cyclic voltammetry was performed at a steady gold disk electrode (d 0.5 mm) at a scan rate of 0.2 V s$^{-1}$. In other experiments the amount of TFP was increased to 4 or 10 equiv.

**Electrochemical procedure for the kinetics of formation of the Pd(0) complex and its reactivity in oxidative addition with PhI**

15 mL of DMF containing $n$Bu$_4$NBF$_4$ (0.3 M) were introduced into the cell followed by 69 mg (0.3 mmol) of TFP and 6.7 mg (0.03 mmol) of Pd(OAc)$_2$ at 25 °C The kinetic measurements for the Pd$^0$ formation were performed at a rotating gold disk electrode (d 2 mm, ω = 105 rad s$^{-1}$) polarized at +0.4 vs SCE. The increase of the oxidation current of Pd$^0$(TFP)$_3$ was recorded until a limiting current was observed ($i_{\text{lim}}$ in text).

Once the Pd(0) was formed, 3.4 µL (0.03 mmol) of PhI were added and the kinetics of the oxidative addition was investigated using the same technique. The decrease of the oxidation current was recorded until total conversion. Other experiments were similarly performed in the presence of 12.5 µL (0.09 mmol) of NEt$_3$ or 90 mg (0.3 mmol) $n$Bu$_4$NOAc added before PhI.

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**References and Footnotes**


8. See Ref 1(2) for the kinetic law.

9. Since the free TFP concentration varied from $6C_0$ to $7C_0$ during the oxidative addition, an average value of $6.5C_0$ was used in Eq 2.

10. From previous work, it has been established that the oxidation potential of $(\text{DMF})\text{Pd}^0(\text{TFP})_2$ (0.34 V) is more positive than that of $(\text{DMF})\text{Pd}^0(\text{PPh}_3)_2$ (0.14 V)\(^6\) which shows that TFP is less electron rich than PPh\(_3\). Note that we are not comparing $E^0$ but $E^\circ$ potentials, so kinetic effects are also involved and not only pure thermodynamics.